Flash pyrolysis properties of algae and lignin residue

Trinh, Ngoc Trung; Jensen, Peter Arendt; Sørensen, Hanne Risbjerg; Dam-Johansen, Kim; Hvilsted, Søren

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

FLASH PYROLYSIS PROPERTIES OF ALGAE AND LIGNIN RESIDUE

Trung Ngoc Trinh [#], Peter A. Jensen[#], Hanne Risbjerg Sørensen[*], Kim Dam-Johansen[#], Søren Hvilsted[#]
[#] Department of Chemical Engineering and Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark.
[*] DONG engery, DONG Energy, Kraftsværksvej 53, DK-7000, Fredericia, Denmark.
Corresponding author: Peter A. Jensen. Tel.: +45 45 25 28 49; E-mail address: PAJ@kt.dtu.dk

ABSTRACT: A fast pyrolysis study on lignin and macroalgae (non-conventional biomass) and wood and straw (conventional biomass) were carried out in a pyrolysis centrifugal reactor. The product distributions and energy recoveries were measured and compared among these biomasses. The fast pyrolysis of macroalgae showed a promising result with on yield of 54 wt% dry ash free basis (daf) and 78% energy recovery in the bio-oil. The physiochemical properties of the bio-oils were characterized with respect to higher heating value, molecular mass distribution, viscosity, pH, density and elemental compositions. The lignin and macroalgae oil properties were quite different to those of the conventional oils.
Key words: fast pyrolysis, lignin, macroalgae, wood, straw, bio-oil properties.

1 INTRODUCTION

Bio-oil obtained from pyrolysis of biomass is considered as an alternative CO_2 neutral fuel. Bio-oil is easily stored and transported and can be used directly as a fuel in boilers or gas turbines, or it can be used as a feedstock to produce chemicals or transportation fuels (1,2). Wood is often found to be an optimal feedstock for fast pyrolysis with a bio-oil yield of 70 – 75 %wt (1,2). However, other alternative biomass feedstock may be applicable. Among the forms of non-conventional biomass: macroalgae and lignin (industrial residue) may be attractive materials for fast pyrolysis due to their low price and non-competitiveness with food crops.

Macroalgae are usually cultivated in coastal areas. Among maroalgae species ulva lactuace is considered as a potential macroalgae for production of biofuel. It can produce up to 45 tons dry/ha/year and has a content of carbohydrates of up to 60% of dry matter (3). The production of the macroalgae is estimated to be 2 – 20 times higher than the production potential of terrestrial biomass per unit surface area (3,4). The macroalgae often have a high ash content (10 % – 40 wt%) containing larger amount of alkali metals, chloride and sulfur (3,4,5). This will probably cause slagging, fouling and aerosol formation related problems for the potential uses of the algae in combustion and gasification plants (9). However, fast pyrolysis is performed at a lower temperature compared to combustion or gasification, and it is believed that the process may not be significantly disturbed by the ash. Most metal elements will probably be concentrated in the char (7,8). Although macroalgae has been recognized as a promising feedstock for fast pyrolysis processes, no study regarding macroalgae fast pyrolysis has been performed to evaluate this potential. So far, studies of macroalgae pyrolysis carried out in a fix bed reactor has been reported (6,21). These studies showed bio-oil yields of 13 – 47 wt% (39 – 61 wt% daf) obtained from various macroalgae spices.

Lignin is the second most abundant biomass component and is a complex, amorphous cross-linked and three-dimensional, highly branched polymer (10). Lignin is mainly produced by the pulp and paper industry and in the near future it will also appear as a by-product from the bio-ethanol industry. The potential of lignin produced as a residue in the paper industry is more than 50 million tons/year. But only about 2% of the lignin residue is used as commercial products for producing lignosulphonates and kraft lignins (11). Most of lignin is burned to generate energy for the pulp mills. Since the fast pyrolysis has been developed for bio-oil production from biomass, the lignin may be used as a feedstock for this process to produce a higher value product such as bio-oil that may be used as a liquid fuel, petrochemical phenol, adhesives, resins or to polymer application. Some studies have been conducted on lignin fast pyrolysis (12,13). However, the obtained bio-oil yield from lignin pyrolysis has been found to be much lower than that of typical biomasses (12,13). In addition, the work of an international collaboration (13) on the lignin fast pyrolysis figured out that highly concentrated lignin material is difficult to process in a fluidized bed reactor because of blockages at screw feeder.

Different fast pyrolysis reactors such as bubbling fluidized bed reactors, circulating fluidized bed reactors, rotary cone reactors, auger reactors and ablative reactors have been developed and are close to commercialization (1). The main difference among these reactors is that different heat transfer methods are used to obtain immediately a high heating rate. The pyrolysis centrifugal reactor (PCR), a type of ablative reactor, has been developed at the CHEC center at the Technical University of Denmark (DTU). By a high centrifugal force, biomass particles can gain a high heating rate of 200 – 2000 K/s (14). The main advantages of this concept compared to fluid bed reactors are a compact design that uses a low flow rate of carrier gas and can treat relatively large biomass particles up to a size of 20 mm. Studies of pyrolysis conditions on the PCR of wood, straw and sewage sludge (8,14,15) have figured out that temperatures around 525 – 575 ºC and gas residence time around 0.8 s should be used to obtain maximum bio-oil yield

There is a paucity of lignin and macroalgae fast pyrolysis for bio-oil production and bio-oil properties in the literature (6,12,13). Previous investigations were concerned on the pyrolysis conditions needed to obtain a maximum bio-oil production. Thus, an overall comparative investigation of fast pyrolysis of lignin, macroalgae, wood and straw are reported in this study. Besides, since the wood, straw, lignin and macroalgae show a variety of biomass compositions especially with respect to ash and lignin contents, the results of this paper can also contribute with knowledge on the influence of the biomass compositions on pyrolysis and bio-oil properties.

2 EXPERIMENTAL SECTION

2.1 Experimental apparatus

The pyrolysis centrifugal reactor (PCR) was developed at the CHEC center (Technical University of Denmark) and is described in detail elsewhere (14). A sketch of the PCR is presented in figure 1. The pyrolysis of biomass takes place inside the reactor, whereby char, bio oil and gas are produced. The char particles are collected by cyclones. The bio-oil is condensed in a bubble chamber filled with isopropanol as a condensing solvent. The temperature in the bubble chamber is controlled to be 30 – 40 °C by means of a cooling water system. The light oil fraction and aerosols are further condensed by a coalescer filled with rockwool. A recycled gas product is pumped back to maintain a desired gas residence time of 0.5 – 2 s in the reactor. Before entering the reactor, the gas is heated up to around 550 °C. The gas products are dried by a water condenser and a gas filter to totally remove liquid before entering a gas meter.

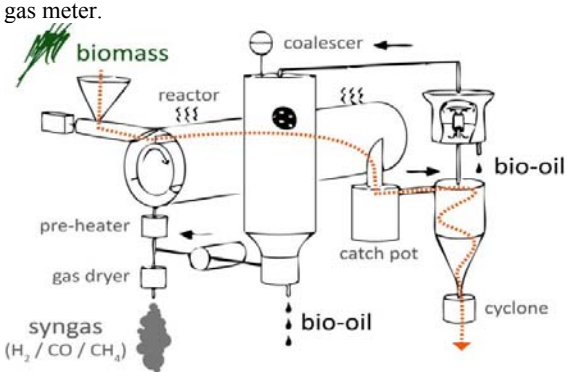

Figure 1: The sketch of the pyrolysis centrifugal reactor (PCR)

The liquid fraction collected from the bubble chamber, coalescer and water condenser is filtered through a whatman filter paper (pore size of 5 µm). The char left on the filter is washed thoroughly by ethanol and then dried in an oven at 100 °C. The bio-oil yield is determined from the liquid that passed through the filter paper. The char yield is determined from the chars collected in the cyclones and the char left on the filter paper. The gas measured from the gas meter is used to calculate the gas yield by the ideal gas equations.

The pyrolysis of the wood, straw, lignin and algae were performed on the PCR with constant conditions: an rotor speed of 8870 rpm, a gas residence time of 0.8 second, a total experimental time of 60 - 90 minutes, feed consumption of 350 - 750 g biomass for each run and feeding rate of 340 – 990 g/hour. The experiments were performed twice with each biomass to ensure reproducible pyrolysis products determinations. The obtained mass balance closures were in the range of 93 – 99 %.

2.2 Characterization of the biomasses

The applied lignin sample was a solid residual from a straw ethanol plant and provided by Inbicon A/S, DONG Energy, Denmark. The macroalgae (ulva lactuce) was cultivated from May to September 2008 in a land-based facility at the Danish Shellfish Center, Nykøbing Mors and provided by the Danish Technological Institute, Denmark. The wheat straw and beech wood were from Danish fields and woods. All biomasses have particle sizes of less than 1 mm.

The biomass samples were measured by the following methods: the moisture content by ASTM D2216, the ash content by ASTM D1102 – 84, higher heating value by a bomb calorimeter (IKA C-200).

The element contents of the wood, lignin and algae samples were analysed by flash combustion (Thermo Finnigan, Flash EA1112) for CHN, by ICP-OES axial for Cl and S, and by ICP-OES radial for Al, Fe, P, Si, Ca, Mg, K, Na. The oxygen content was calculated by difference. The elemental contents of the straw and straw oil were adopted from the reference (15) where the straw was pyrolysed on the PCR at the same conditions as in this work. The elemental contents provided from reference 15 were analysed by wavelength dispersive X-ray fluorescence spectrometry (WXRF).

Thermalgravimetric analysis (TGA) of the biomasses were carried out in the temperature range of 100 – 1000 °C and at a constant heating rate of 10 °C /min in a N_2 flow using a TGA instrument (Netzsch STA 449 F1).

The biomass components were analysed following the NREL protocols: a determination of extractives in the biomasses by NREL/TP-510-42619 (17) and a determination of the structural carbohydrates and lignin in biomass by NREL/TP-510-42618 (18). The biomasses were extracted in water and ethanol for determination of extractives. The biomasses were diluted in a strong acid for determination of structural carbohydrates and lignin. The lignin content was determined as the residue left after acid digestion while soluble aliquot was used to analyze holocellulose such as glucan, xylan, glactan, manna, arabinan and rhamnan by a HPLC (Shimadzu Prominence - HPLC, Shimadzu Corporation, Kyoto, Japan, the refractive index detector (RID-10A)) with an Aminex HPX-87H Ion Exclusion column (Bio-Rad Laboratories, USA) (eluent 12 mM H_2SO_4, flow 0.6 ml/min, column temp 63 ºC) used for the straw, lignin and algae and an Aminex HPX-87P (Bio-Rad Laboratories, USA) (eluent water, flow 0.5 ml/min column temp 80 ºC) used for the wood.

2.3 Characterization of the bio-oils

The isopropanol solvent was removed from the liquid samples collected from the PCR by a rotary vacuum evaporator at 30 °C to obtain the bio-oil samples. About 1 – 8 wt% water content and small amounts of volatiles of bio-oil samples were probably lost during the solvent removal.

The water content was determined by a Karl Fischer titration (Metrohm-701KT titrino). The higher heating value (HHV) was measured by a bomb calorimeter (IKA C-200). The viscosity was determined by rotational viscosimer (PAAR AMV 200). The density was measured by density meter (Anton paar – DMA 4100). The pH was determined by pH meter (PHM 92, Lab pH meter).

The elements concentrations were analysed by the following methods: C, H, N by flash combustion (Thermo Finnigan, Flash EA1112), Cl and S by ICP-OES axial, and Al, Fe, P, Si, Ca, Mg, K, Na by ICP-OES radial and the oxygen content was calculated by difference.

The molecular weight distribution was analyzed by Size-exclusion chromatography (SEC) using the following instrument: viscoteck GPCmax VE-2001 equipped with Viscotek TriSEC Model 302 triple

detector using two PLgel mixed-D columns from Polymer Laboratories. The samples were run in THF at 30 °C (1mLmin^{-1}). The molar-mass characteristics were calculated using polystyrene standards. In order to take a representative sample for GPC analysis the bio-oils were diluted with ethanol to make it homogeneous and then passed through a 0.2 μm filter.

3 RESULTS AND DISCUSSION

3.1 Characterization of the biomasses

The results of the proximate analysis, ultimate analysis and element analyses of the biomasses are presented in table I. The volatile yield is in the range of 84 - 76 wt% db for the wood and the straw whereas a relative yield of 67 – 61 wt% dry basis (db) for the algae and lignin are determined. The ash contents are in the low range of 3 – 6 wt% db for the wood and straw and in the high range of 12 – 29 wt% db for the lignin and algae. The alkali metals act as catalyst of biomass pyrolysis and they have a strong effect on the product yields and oil compositions (1,20,22,23). The lignin shows the highest carbon and the lowest oxygen content, resulting in the lowest of O/C ratio when compared to the other biomasses. A low O/C value has found to give a relative high higher heating value (HHV) (22). Thus this could explain the highest HHV value is obtained for the lignin. The wood, straw and algae have similar contents of the carbon, oxygen and O/C ratios.

Table I: The approximate analyses of the investigated biomasses

	Wood	Straw[(a)]	Lignin	Algae
Proximate analysis (%wt)				
Moisture (%wt)	9.1	7.9	4.7	8.9
Volatile (% wt db)	84.3	75.8	61.2	67.1
Fixed carbon (% wt db)	13	18.4	26.7	9.3
Ash (% wt db)	2.7	5.8	12.1	29.1
HHV (MJ/kg on as receiver)	19.0	18.4	22.8	12.9
HHV (MJ/kg on daf)	21.5	21.3	27.4	20.8
Ultimate analysis (%wt daf)				
C	52.7	46.8	65.8	45.3
H	5.9	6.7	6.5	6.87
O	41.0	44.6	26.8	38.0
N	0.22	1.2	1.4	4.5
Cl	< 0.01	0.64	0.023	1.5
S	0.02	0.2	0.16	4.6
O/C	0.78	0.95	0.41	0.84
Element analyses (%wt db)				
Al (%wt)	0.054	0.028	0.069	0.29
Fe (%wt)	0.052	0.028	0.30	0.31
P (%wt)	0.014	0.14	0.064	0.34
Si (%wt)	0.84	1.34	4.18	4.10
Mg (%wt)	0.035	0.090	0.022	2.52
Ca (%wt)	0.32	0.37	0.43	2.74
K (%wt)	0.14	1.73	0.13	2.45
Na (%wt)	0.018	0.021	0.28	0.23

(a) the element analyses of the straw were adopted (15)

Among the biomasses algae was observed to have higher nitrogen, sulfur, chloride and alkali contents than that of the other feedstocks. The lignin was collected from a straw ethanol plant thus it was treated and washed several times, consequently although the lignin has the high ash content, it contains a relatively low chlorine and alkali contents.

Table II. The biomass compositions

	On dry ash free basis			
Component	Wood	Straw	Lignin	Algae
Extractives	1.0	7.0	0.0	40.5
Klason lignin	24.5	18.0	78.8	13.8
Holocellulose	62.0	65.4	11.2	25.7
Glucan	40.1	40.8	8.3	8.5
Xylan	17.6	21.9	2.7	6.7
Galactan	1.6	0.0	0.0	0.0
Mannan	1.6	0.0	0.0	0.0
Arabinan	1.0	2.7	0.2	0.0
Rhamnan	0.0	0.0	0.0	10.5
Others	12.6	9.5	10.0	20.0

The results of the analysis of the biomasses organic compositions are summarized in table II. Lignin is a complex, heavily cross-linked and highly branched polymer (10). The decomposition of lignin takes place at higher pyrolysis temperature than those of cellulose and hemicelluloses components. A lignin rich material has been found to produce a relatively low bio-oil yield and a high char yield by the fast pyrolysis (12,13). The wood and straw samples have lignin contents of 25 and 18 wt% daf, respectively. While the lowest lignin content of 14 wt% daf was observed for the algae sample and the highest lignin content of 79 wt% daf appeared for the lignin sample. Holocellulose contains major sugars such as glucan, xylan, galactan, mannan, arabinan, rhamnan that are decomposed from cellulose and hemicellulose components. The holocellulose contents are of 62 – 65 wt% daf for the wood and straw, and around 11 – 26 wt% daf for the lignin and algae. The algae shows a large extractive content that is believed to contain a majority of protein and starch (3,21).

The ash (especially the alkali metals) and lignin contents strongly influence the product yields and bio-oil properties. Among the biomasses, there is considerable variation of the ash and lignin contents. It is seen that the algae has the lowest lignin content of 14 %wt daf and the highest ash content of 29 %wt. The lignin has an ash content of 12 %wt and the highest lignin content of 79 %wt daf. The straw sample has an ash content of 6 %wt and a low lignin content of 18 %wt daf. The wood is considered as probably the best feedstock for fast pyrolysis with an ash content of 3 %wt and a lignin content of 25 %wt daf.

Thermal analysis (TGA and DTG) of the biomasses was carried out at a heating rate of 10 ºC/min, up to 1000 ºC under N_2 flow. The thermal conversion pyrolysis of the biomasses are shown in figure 2. The wood and straw experience a major initial mass loss between 200 – 500 ºC, with DTG peak temperatures of 360 ºC for wood and 340 ºC for straw. The lignin experiences pyrolysis conversion in a broad temperature range of 120 – 550 ºC and its DTG peak temperature is 350 ºC. The thermal decompositions of wood, straw and lignin are consistent with lignicellulose biomass pyrolysis data in the literature (12,24,26). The thermal degradation of the algae is distinctly different from that of the lignocellulosic biomasses. The main DTG peak of algae appear at a temperature of 280 ºC, with two shoulders at 340 and 460 ºC and a small peak of 750 ºC. The peaks of protein, starch, cellulose and hemicelluloses are probably

overlapped in the temperature range of 280 – 340 ºC while the peaks at 460 ºC and 750 ºC are believed to be corresponding to decomposition of lignin and a release of inorganic compounds, respectively (21,24,25).

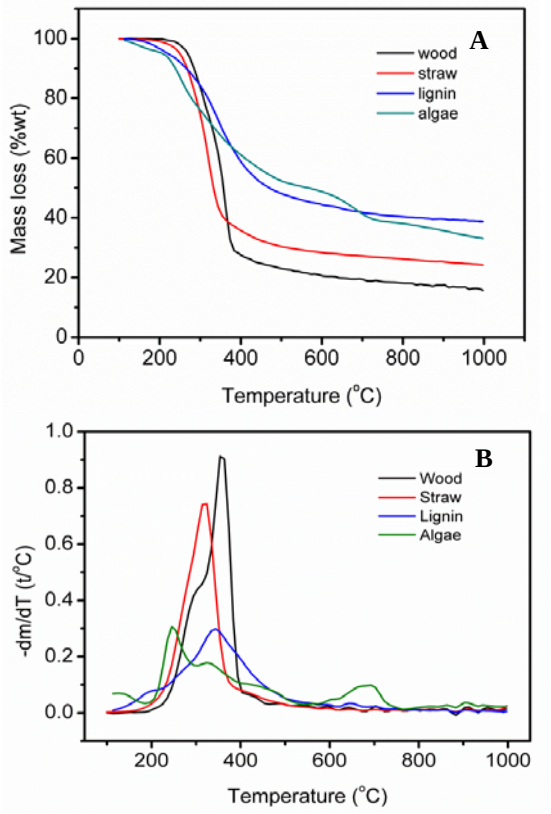

Figure 2: TGA (A) and DTG (B) for pyrolysis of the investigated biomasses

3.2 The fast pyrolysis product distributions

The pyrolysis experiments in the PCR of the biomasses were carried out with a gas residence time of 0.8 s, a reaction temperature of 550 ºC and feeding rates of 340 – 990 g/hour. The temperature is believed to be sufficient to obtain full decomposition of the biomasses (see figure 2B) and using a gas residence time of 0.8 s considerable secondary reactions of tar will probably be avoided. The pyrolysis conditions used have previously provided a maximum bio-oil yield for straw, wood and sewage sludge on the PCR (8,14,15).

The ash influences pyrolysis products distribution of biomasses (1,20,22,23). However the roles of of individual components of ash on the pyrolysis process are not well understood. Alkali metals have been found to catalyse the pyrolysis and have a strong influence on the pyrolysis products distribution (20) whereas silicate seems to be inactive to pyrolysis of biomass. For natural lignocellulosic biomasses the alkali content seems often to be proportional to the ash content (20), thus the effects of alkali metals are considered to be as those of ash. A high feedstock ash content leads to a decrease of the bio-oil yield along with an increase of both the char yield and gas yield (20,22). The relative portions of cellulose, hemicelluloses and lignin in biomass have a major influence on the product distribution and quality of the bio-oil (20,22). The cellulose component mainly contributes to the pyrolysis bio-oil production, while the hemicelllulose component produces a lower bio-oil yield and a higher gas and char yields (28). The lignin component is also found difficult to pyrolyse and produce the lowest bio-oil yield and the highest char yield (12,13).

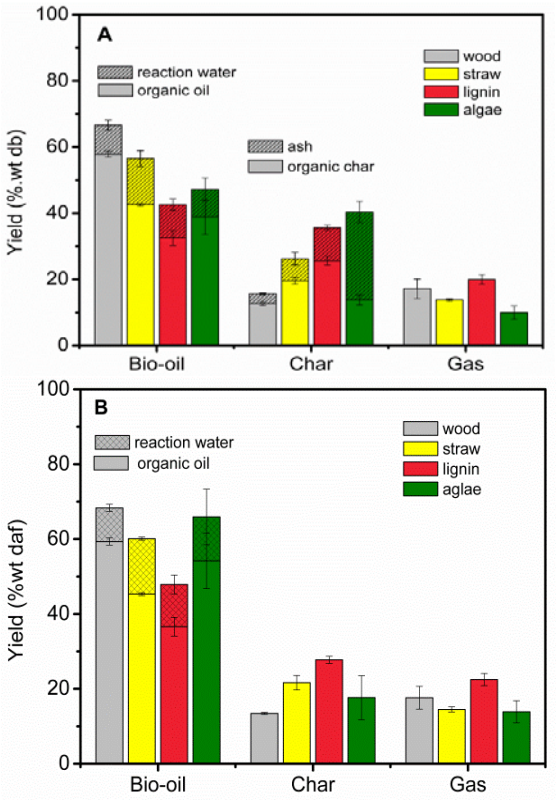

Figure 3: The product distributions of biomass pyrolysis on PCR (A: on dry feedstock basis, B: on dry ash free feedstock basis)

Due to a considerable variation of the ash content in the biomasses, there are differences between the product yields based on the dry feedstock basis and an the dry ash free feedstock basis. The product yields presented on both basises are showed in figure 3. The wood that was the lowest ash content is the best feedstock to produce a high bio-oil yield of 68 wt% daf. The straw with the 5.8 wt% ash content obtained a bio-oil yield of 62 wt% daf. The results are consistent with a linear relationship between bio-oil yield and ash content in a range of 1 – 7 %wt of natural lignocellulosic biomass presented in the literature (20,29). Lignin samples with a higher lignin content have been shown to obtain a lower bio-oil yield (12,13). With a lignin content of 79 wt% daf, the lignin sample provided a bio-oil yield of 48 wt% daf. The algae sample has the lowest lignin content of 13 wt% daf and the highest ash content of 29 wt% with a total K and Na of 2.68 wt%. The obtained bio-oil yield of the algae sample was 64 wt% daf. It is just slightly lower than that of the wood with about 4 wt% and higher than that of the straw with 2 %wt. The pyrolysis of various species macroalgae have been investigated in various fixed bed reactors (6,21). The bio-oil yields obtained were in a range of 57 – 61 wt% daf. In this study, the bio-oil yield obtained from the PCR is slightly higher than that of the fixed bed algae pyrolysis studies (6,21).

Reaction water is formed by the decompositions of biomass cellulose, hemicelluloses, lignin and protein. The

reaction water yield was in a range of 9.8 – 10.1 wt% daf for wood, lignin and algae pyrolysis while the highest of 16.6 %wt daf was observed for the straw pyrolysis (see figure 3). It seems that the alkali, mainly potassium catalyse the formation of reaction water (30), and also the high proportion of cellulose (corresponding to glucan in table 2) probably caused the high straw reaction water. A similar high reaction water yield of 16 wt% db was also reported for straw pyrolysis by Osnaa et al. (22).

The gas yield varied from 8 to 20 wt% daf for the biomasses. The highest char yield of 28 %wt daf was obtained by the lignin sample while the lowest char yield of 12 %wt daf appeared from the wood sample. The char yield was around 20 wt% daf for the algae and straw feedstocks.

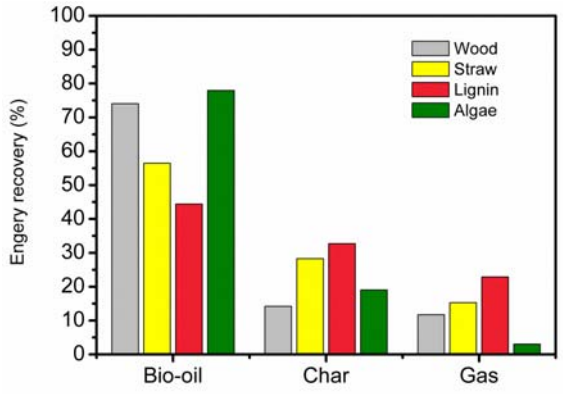

Figure 4: The energy recovery of gas, bio-oil and char

The oil and the char energy recovery were calculated based on the product yields and their heating values. The gas energy recovery was calculated by difference. The results are shown in figure 4. With a high organic oil yield of 58 wt% daf, wood oil gained a 74 % energy recovery whereas the straw and lignin oils contained 56 wt% and 45 wt%, respectively of the feedstock energy content. An interesting result was found regarding the algae sample, the organic oil yield was 54 wt% daf, but the algae oil recovers 78 % of the feedstock energy content. The fast pyrolysis process may be a promising way to upgrade algae to a liquid fuel because of this high energy recovery efficiency.

3.3 Characterization of the bio-oil properties

The heating value, pH, density and elemental content of the investigated bio-oils are presented in table III. The HHV of the wood oil and straw oil had similar values of around 24 MJ/kg on dry basis. The HHV of the algae oil and the lignin oil show a higher value of 26 and 30 MJ/kg, respectively. The pyrolysis biomasses produce organic acids (7,31), causing the bio-oils to have pHs of about 2 to 4 (29,31). The pHs of the investigated bio-oils vary from 3.2 to 4.3. The pH of the algae oil was slightly higher than those of the lignocellulosic oils. Highly acidic oils may cause corrosions of steel. Thus storage of the oils should be in acid-proof materials like stainless steel or polyolefins. The density of the investigated oils were 0.98 -1.15 g/ml.

The lignin oil and the algae oil have carbon contents of 60 - 66 wt% db and oxygen contents of 25 - 28 wt% db. In contrast the wood oil and straw oil have lower carbon contents of around 57 wt% and higher oxygen contents of around 35 wt%. The differences in the carbon and oxygen contents of the oils are probably related to the glucan component of the biomass that is the main component of cellulose degradation in a strong acid solution. Cellulose degradation at pyrolysis condition produces a majority of mono sugars and levoglucosans (22,31) that have a high oxygen content. Thus a high cellulose content (high glucan content) of the wood and straw probably causes the high oxygen contents in the bio-oils.

In this study, the algae oil was found to have a high nitrogen content (4 wt% db), a sulfur content of 0.77 wt% db and a chloride content of 0.64 wt% db. If the oil is used for combustion the nitrogen, sulfur and chlorine may cause corrosions of boilers and environmental problems related to NOx, SO_2 and HCl emissions. This indicates that a further treatment to reduce the N, Cl and S may be necessary if the algae oil shall be applied for industrial combustion applications.

Table III: The bio-oil properties

	Bio-oil			
	Wood	Straw[a]	Lignin	Algae
Water content (%wt)	27.3	25.7	27.5	26.6
HHV (MJ/kg) on wet basis	17.4	17.6	21.5	18.9
HHV (MJ/kg) on db	24.0	23.7	29.7	25.7
pH	3.2	3.8	3.9	4.3
Density @40 °C (g/ml)	1.12	1.15	1.09	0.98
Element content (wt% db)				
C	57	56.9	65.6	59.5
H	7.2	5.9	8	7.2
O	35.2	35.2	24.5	28
N	0.5	1.7	1.7	4
S	0.04	0.15	0.18	0.77
Cl	0.01	0.17	0.03	0.64
H/C	0.13	0.10	0.12	0.12
O/C	0.62	0.62	0.37	0.48

Bio-oil is known to contain some phenolics that are still reactive and will polymerize to form oligomers with molecular weights as high as 5000 or more (16). The polymerization, the aging, may take months or years. The most typical method to measure the aging of bio-oils is to use an accelerated aging procedure. In the present study, the bio-oils were placed in a tightly closed container and heated in an oven for 24 hours at 80 ºC (19,27). The aged bio-oil samples are relevant to that of oil stored in a year at room temperature (27). Figure 5 shows molecular weight distributions of original and aged oils of wood, straw, lignin and algae. The molecular mass distribution of original bio-oils shows two main peaks at around 165 and 398 g/mol for the bio-oils of wood, straw and lignin. While the algae oil has another third shoulder at around 1260 g/mol together with two main peaks at 165 and 320 g/mol. The bio-oils produced on the PCR have mean molecular weights in a range of 404 – 455 g/mol (see table IV) that are consistent with other studies (20,32). The mean average molecular weights of the lignin oil and algae oil are 1.13 times higher than that of the wood and straw oil. It is probably that the higher lignin derivatives in the lignin and higher starch and protein derivatives in the algae oil cause of the difference.

The difference in mean molecular weight of the wood oil, straw oil and algae oil corresponds to viscosities of 16 , 25 and 101 mPa.s, respectively (see table IV). The viscosity measurement of the lignin oil presented some difficulties. In order to understand the viscosity of the lignin oil, the sample was turbulently mixed and then kept immobile for a hour. The top and bottom phases were taken to the viscosity measurements. As a result, the

viscosities of the top and the bottom samples are 9.4 and 102 m.Pa.s, respectively.

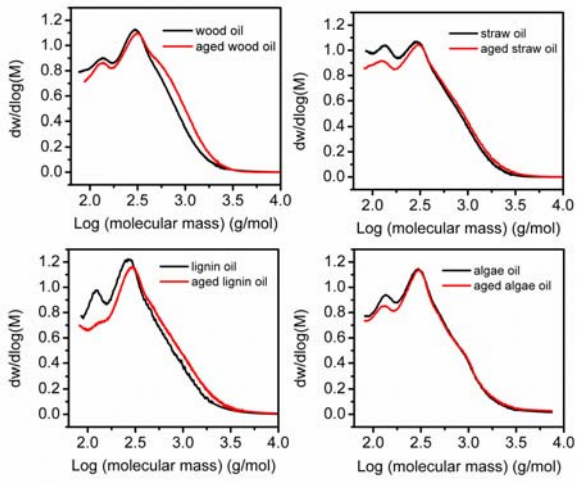

Figure 5: The molecular mass distribution of bio-oils

Table IV: The mean molecular weight of the original oils and aged oils

	Bio-oil			
	Wood	Straw	Lignin	Algae
Mean molecular mass (g/mol)	404	405	451	455
Mean Aged molecular mass (g/mol)	462	453	574	482
% increase of mean molecular mass	14	12	27	6
Viscosity@ 40 ºC (mPa.s)	16.1	25.0	9.4[a] 102.1[b]	100.9

[(a)] the viscosity of top sample,[(b)] the viscosity of bottom sample

As can be seen in figure 5, the aged oils have a similar molecular weight patterns as the original oils. A decreased proportion of the low molecular mass fraction with molecular weight less than 320 g/mol and an increased proportion of higher than 320 g/mol fraction were clearly observed between the original oils and the aged oils. Chaala et al. (19) studied the aging of a softwood bark oil and found that the aged oil had a considerable change of the faction with molecular mass higher than 1000 g/mol and the faction with molecular mass lower than 300 g/mol. The mean molecular weight of the aged bio-oil enhances 12 – 27 % for the lignocellulosic oils and 6 % for the algae oil (see table IV).

4 CONCLUSION

In this work fast pyrolysis PCR experiments were conducted with algae and lignin to produce bio-oils. The PCR pyrolysis is a promising method to produce bio-oil from high ash-biomasses, which are difficult to process effectively in combustion or gasification reactors.

The algae pyrolysis showed promising results with a bio-oil yield of 66 %wt daf and an energy recovery in the bio-oil of 78%. These results are similar to that of wood pyrolysis. While the lignin pyrolysis shows a much lower bio-oil yield of 48 wt% daf and an energy recovery in the bio-oil of 45 %. The lignin and macroalgae oil properties were quite different to those of the straw and wood bio-oil. The main differences observed in the product yields and the bio-oil properties can be partially explained by differences of the biomass compositions especially differences with ash and lignin contents of the feedstocks.

ACKNOWLEDGEMENTS

Financial support of this PhD study by DONG energy A/S, Energinet.dk and DTU is gratefully acknowledged. The authors are very grateful to Tran Thuong Dang, Kim Chi Szabo and Ingelis Larsen from Chemical and Biochemical Engineering Department, Technical University of Denmark who have performed some of the analyses reported in this paper.

REFERENCES

[1] E. Butler, G. Devlin, D. Meier and K. McDonnell, A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading, Renewable and Sustainable Energy Reviews, Vol. 15, (2011) pag. 4171.

[2] A. V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, Vol. 38, (2012) pag. 68.

[3] L. Nikolaisen, P.D. Jensen, K.S. Bech, J. Dahl, J. Busk, T. Brødsgaard, M.O. Rasmussen, A. Bruhn, A. Bjerre A, H.B. Nielsen, K.R. Albert, P. Ambus, Z. Kadar, S. Heiske, B. Sander, E.R. Schmidt, Energy Production from Marine Biomass (ulva lactuca) PSO Project No. 2008-1-0050, 2011, Danish Technological Institute, Denmark

[4] A.B. Ross, J.M. Jones, M.L. Kubacki and T.Bridgeman, Classification of macroalgae as fuel and its thermochemical behaviour, Bioresource Technology, Vol. 99, (2008), pag. 6494.

[5] D. Li, L. Chen, X. Zhang, N. Ye, and F.Xing, Pyrolytic characteristics and kinetic studies of three kinds of red algae, Biomass and Bioenergy, Vol. 35,(2011), pag. 1765.

[6] Y.J.Bae, C.Ryu, J.K.Jeon, J.Park, D.J. Suh,Y.W. Suh, D.Chang and Y.K.Park, The characteristics of bio-oil produced from the pyrolysis of three marine macroalgae, Bioresource Technology, Vol. 102, (2011), pag. 3512.

[7] W.J.DeSisto, N. Hill, S.H.Beis, S.Mukkamala, J.Joseph, C.Baker, T.H.Ong, E.A.Stemmler, M.C.Wheeler, B.G. Frederick and A.van Heiningen, Fast Pyrolysis of Pine Sawdust in a Fluidized-Bed Reactor, Energy & Fuels, Vol. 24, (2010), pagp. 2642.

[8] N. T.Trung, P.A.Jensen, and K.Dam-Johansen, The influence of pyrolysis temperature on sewage sludge pyrolysis products distribution, bio-oil and char properties, CHEC report, 2012

[9] B.M.Jenkins, L.L. Baxter, J. Miles and T. R. Miles, Combustion properties of biomass, Fuel Processing Technology, Vol. 54, (1998), pag. 17.

[10] M.P.Walsh, Highway Vehicle Activity Trends and Their Implications for Global Warming: The United States in an International Context. In Transportation and Energy: Strategies for a Sustainable Transportation System; American Council for an Energy-Efficient Economy: Washington, DC, 1995.

[11] G.J.A. osselink, E.de Jong, B.Guran, B and Abächerli, A., " Co-ordination network for lignin—standardisation, production and applications adapted to market requirements (EUROLIGNIN)," Industrial Crops and Products, Vol. 20, (2004), pag.121.
[12] P.J. de Wild, W.J.J. Huijgen, and H. J. Heeres, Pyrolysis of wheat straw-derived organosolv lignin Journal of Analytical and Applied Pyrolysis, Vol. 93, (2012) pag. 95.
[13] D. J. Nowakowski, A. V. Bridgwater, D. C. Elliott, D. Meier, and P. de Wild, Lignin fast pyrolysis: Results from an international collaboration, Journal of Analytical and Applied Pyrolysis, Vol. 88, (2010), pag. 53.
[14] N. Bech, M. B. Larsen, P. A. Jensen, and K. Dam-Johansen, Modelling solid-convective flash pyrolysis of straw and wood in the Pyrolysis Centrifuge Reactor, Biomass and Bioenergy, Vol. 33, (2009), pag. 999.
[15] N. Bech, Insitu flash pyrolysis of straw. PhD thesis. (2008), Department of chemical engineering, DTU. Kgs. Lyngby, Denmark
[16] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, and C. Roy, Characterization of bio-oils in chemical families, Biomass and Bioenergy, Vol. 31, (2007), pag. 222.
[17] R. Sluiter, C. Ruiz, J. Scarlata, J. Sluiter, and D. Templeton. Technical Report NREL/TP-510-42619. Determination of Extractives in Biomass. Laboratory Analytical Procedure (LAP). Issue Date: 7/17/2005
[18] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, and D. Crocker. Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42618 Issue Date: April 2008.
[19] A. Chaala, T. Ba, M. Garcia-Perez, and C. Roy, Colloidal Properties of Bio-oils Obtained by Vacuum Pyrolysis of Softwood Bark: Aging and Thermal Stability, Energy & Fuels, Vol. 18, (2004), pag. 1535.
[20] R. Fahmi, A. V. Bridgwater, I. Donnison, N. Yates, and J. M. Jones, The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability, Fuel, Vol. 87, (2008), pag. 1230.
[21] B. Maddi, S. Viamajala, and S. Varanasi, Comparative study of pyrolysis of algal biomass from natural lake blooms with lignocellulosic biomass, Bioresource Technology, Vol. 102, (2011), pag. 11018.
[22] A. Oasmaa, Y. ê Solantausta, V. Arpiainen, E. Kuoppala, and K. Sipila, Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues, Energy & Fuels, Vol. 24, (2009), pag. 1380.
[23] N. Abdullah and H. Gerhauser, Bio-oil derived from empty fruit bunches, Fuel, Vol. 87, (2008), pag. 2606.
[24] L. Sanchez-Silva, D. López-González, J. Villaseñor, P. Sánchez and J. L. Valverde, Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis, Bioresource Technology, Vol. 109, (2012), pag. 163.
[25] A. B. Ross, K. Anastasakis, M. Kubacki and J. M. Jones, Investigation of the pyrolysis behaviour of brown algae before and after pre-treatment using PY-GC/MS and TGA, Journal of Analytical and Applied Pyrolysis, Vol. 85, (2009), pag. 3
[26] C. E: Greenhalf, D. J. Nowakowski, A. V. Bridgwater, J. Titiloye, N. Yates, A. Riche, and I. Shield, Thermochemical characterisation of straws and high yielding perennial grasses, Industrial Crops and Products, Vol. 36, (2012), pag. 449.
[27] A. Oasmaa and E. Kuoppala, Fast Pyrolysis of Forestry Residue. 3. Storage Stability of Liquid Fuel, Energy & Fuels, Vol. 17, (2003), pag. 1075.
[28] D. K. Shen, S. Gu, and A. V. Bridgwater, The thermal performance of the polysaccharides extracted from hardwood: Cellulose and hemicellulose, Carbohydrate Polymers, Vol. 82, (2010), pag. 39.
[29] R.H. Venderbosch, and W. Prins, Fast pyrolysis technology development, Biofuels, Bioproducts and Biorefining, Vol. 4, (2010), pag. 178.
[30] M. Coulson, Pyrolysis of perennial grasses from southern Europe. Thermalnet Newsletter (2006), 2, pag 6.
[31] A. M. Azeez, D. Meier, J. ê. Odermatt and T. Willner, Fast Pyrolysis of African and European Lignocellulosic Biomasses Using Py-GC/MS and Fluidized Bed Reactor, Energy & Fuels, Vol. 24, (2010), pag. 2078.
[32] L. Ingram, D. Mohan, M. Bricka, P. Steele, D. Strobel, D. Crocker, B. Mitchell, J. Mohammad, K. Cantrell and C. U. Pittman, Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils, Energy & Fuels, Vol. 22, (2007), pag. 614.